PATENT ABSTRACTS OF JAPAN

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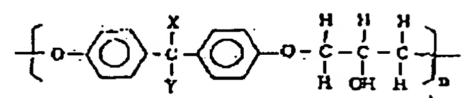
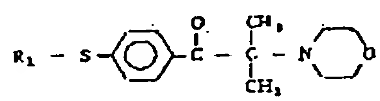
(54) POLYETHERIMIDE FILM HAVING ADHESIVE LAYER

(57)Abstract:



I



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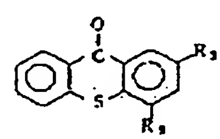

III

PURPOSE: To obtain the title film which has excellent adhesiveness and workability in bonding, and will not warp when laminated, by forming a layer of an adhesive comprising a specified phenoxy resin on a polyetherimide film.

CONSTITUTION: A polyhydric phenol is made to react with epichlorohydrin to give a phenoxy resin (a) of the formula (wherein X and Y are each H or alkyl), which comprises a polyhydroxy polyether having a number-average molecular weight of 5,000 or higher and a weight-average molecular weight of 30,000 or higher. Component (a) is mixed with a (meth)acrylate prepolymer or monomer (b) having ethylenic double bonds and a photopolymerization initiator (c) {e.g., a compound of formula II [wherein R1 is H, (hydroxy)alkyl, aryl, phenyl, tolyl, cyclohexyl or mercaptoalkyl ether]}, if required, together with a photosensitizer [e.g., a compound of formula III (wherein R2 and R3 are each H or alkyl)], thus giving a phenoxy resin solution (B). Component B is applied to a polyetherimide film (A) of a thickness of 25W125μm and dried to form a film of a thickness of 10W30μm thereon.

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法を提案した。然しながらこれらの方法は反りのない積層体は得られるものの接着強度という観点から不満足であることと、アクリルプレポリマー、アクリルモノマーといった比較的低分子組成物であるため初期粘着力に欠け接着作業性の点で難点があるとの2つの問題を改善しなければならないことが判った。

〔発明の目的〕

本発明は従来得られなかった、ラミネート時に反りを生ぜず、強固な接着性が得られるフィルム状接着剤層を有するポリエーテルイミドフィルムを提供せんとする目的で鋭意検討を行った結果、フェノキシ樹脂中に光硬化可能な樹脂組成物が均一溶解せしめられた接着剤層とポリエーテルイミドフィルムからなる構成のものが本目的に合致するとの知見を得、これに基づき研究を進めて本発明を完成するに到ったものである。

〔発明の構成〕

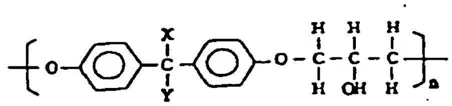
本発明は光重合性組成物を含有するフェノキシ樹脂フィルム層が表面に形成されたことを特徴とするポリエーテルイミドフィルムである。

本発明に用いられるポリエーテルイミドフィルムは押出し法、流延法等の一般的方法で得られるフィルムであればすべて使用可能である。

またフィルムの厚みは適用される用途により異なるが通常25～125μm程度のものが用いられフェノキシ樹脂フィルム形成面を、サンドブラスト法、コロナ放電法、プラズマ照射法等の手法を用いて、粗化せしめることも接着性向上の上から有効な手法である。

該フィルム片面にフィルム状接着剤層が形成されるがその形成法は、光硬化性組成物を溶解含有するフェノキシ樹脂溶液を塗布して乾燥し塗膜を形成して得られる。

この際用いられるフェノキシ樹脂はビスフェノールAまたはビスフェノールF等の多価フェノール類とエピクロルヒドリンより合成される高分子量ポリヒドロキシポリエーテルであり次式の構造を有する熱可塑性樹脂である。



（XおよびYは水素原子またはアルキル基である）

該樹脂は数平均分子量で5,000以上、重量平均分子量で30,000以上の高分子量ポリヒドロキシエーテルであり、その骨格に水酸基を数多く有しているため各種被着体との接着性に優れ、且つ高分子量であるため溶液からの造膜性に優れ強度のある均質のフィルム形成が可能である。加えて熱可塑性であるため熱溶融可能なフィルムであり所謂ホットメルト接着性に優れている。

しかしながら反面該樹脂を単独で用いた場合、耐熱性、耐溶剤性等に劣り本発明の目的とする用途との適用は制限を受けざるを得ない。

又該樹脂の数平均分子量5,000以下、重量平均分子量30,000以下のものであれば、フィルム状の接着剤層としたとき、強度、フィルム造膜性及び収縮性の面から不適当である。該フェノキシ樹脂を溶解し得る溶剤に溶解せしめ樹脂溶液を得た後光硬化可能な組成物を該溶液に均一溶解せしめる。光硬化組成物は、エチレン性2重結合を有する、ウレタンアクリレート、エポキシアクリレート、ポリエステルアクリレート等から選択された1種または2種以上のアクリル又はメタアクリルプレポリマー、アクリル又はメタアクリルモノマー、光開始剤を主成分として形成される。

これら組成物のフェノキシ樹脂への添加割合は組成物の種類、ラミネート温度、硬化物の耐熱・耐薬品性等を勘案して適宜決定される。然しながら塗布乾燥後粘着性を示さない程度の添加であって且つ必要性能を維持する添加割合であることが好ましく固形のエポキシアクリレート、プレポリマー等を単独もしくは併用して用いることが本発明達成の上から好ましい。

光重合開始剤としてはベンゾインイソプロピルエーテル、2－エチルアントラキノン、ベンジル等の如く通常用いられるものが使用可能であるがポリエーテルイミドフィルム透過光で反応せしめる上でチオキサントン系化合物、メロシアニン、

中に1時間浸漬したが、接着剤層には何らの変化も認められなかった。

尚、このときの接着剤層の厚みは25μであった。

比較例1

実施例のフェノキシ樹脂溶液	100重量部
メチルセロソルブアセテート	50 〃
酢酸ブチル	150 〃

上記のようなフェノキシ樹脂溶液を接着剤組成物として、実施例と同様に125μ厚のポリエーテルイミドフィルムと35μ厚の銅箔との接着複合体を得た。只し、この場合は高圧水銀灯による光照射は行なわなかった。

得られた接着複合体の接着強度は初期状態では1.5kgf/cmであったが、200℃、1時間の加熱処理を施こすとポリエーテルイミド面と接着剤層との間で大きな浮きが全面に発生した。

また、銅箔をエッチング除去したフィルムをアセトン中に10分間浸漬したところ、接着剤層を溶解した。

実施例と同様にポリエーテルイミドフィルム上に塗布、乾燥した後に、接着剤層と銅箔の酸化面とが接するように、200μの間隙を有する一対のロール間を室温で通した。このとき過剰の接着剤成分はロールの後ろに絞り出されてしまい、また接着剤層の厚みは15～40μとバラツキが生じた。

実施例と同様な条件で光照射を行なって硬化を完了させたのち、接着強度を測定したところ、初期状態で0.8～1.2kgf/cm、200℃、1時間処理後で0.6～1.0kgf/cmと実施例と比較すると小さな値しか得られなかった。

比較例3

実施例で調製したフェノキシ樹脂溶液	100重量部
トリレンジイソシアネート	3 〃
ジブチル錫ジラウレート	0.001 〃
酢酸ブチル	17 〃

上記接着剤組成物を実施例と同様にポリエーテルイミド上に塗布、乾燥し、銅箔にラミネートした。このラミネート物には光照射を行なわず、150℃にて2時間加熱して接着剤層の硬化を施こした。この接着複合体を室温まで冷却すると、銅とポリエーテルイミドフィルムとの熱膨張係数の差に起因して、ポリエーテルイミド面を内側に大きく反ってしまった。

尚、このときの接着剤層の厚みは30μであった。

比較例2

フェノキシ樹脂を含有しない下記接着剤組成物を調製した。

固形エポキシアクリレートプレポリマー（昭和高分子㈱製商品名リポキシVR－60）	100重量部
ウレタンアクリレートプレポリマー（日本合成化学工業㈱製商品名ゴーセラックUV－3000B）	400 〃
ペンタエリスリトールトリアクリレート	67 〃
チバガイギー社製商品名イルガキュア－907	10 〃
2,4－ジエチルアントラキノン	8 〃
メチルセロソルブアセテート	500 〃
酢酸ブチル	670 〃

特許出願人

住友ベークライト株式会社

US005475048A

United States Patent [19]

Jamison et al.

[11] Patent Number: 5,475,048

[45] Date of Patent: Dec. 12, 1995

[54] CONDUCTOR-FILLED THERMOSETTING RESIN

[75] Inventors: William L. Jamison, Fishers, Ind.; Andrzej Moscicki, Lodz, Poland

[73] Assignee: Thermoset Plastics, Inc., Indianapolis, Ind.

[21] Appl. No.: 163,398

[22] Filed: Dec. 7, 1993

Related U.S. Application Data

[63] Continuation of Ser. No. 863,452, Apr. 3, 1992, abandoned.

[51] Int. Cl.[6] C08K 3/08; H01B 1/02

[52] U.S. Cl. 524/439; 524/440; 252/511; 252/512; 252/513; 252/514

[58] Field of Search 524/439, 440; 252/511–514; 525/193

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Primary Examiner—Tae H. Yoon

Attorney, Agent, or Firm—Barnes & Thornburg

[57] ABSTRACT

Conductor-filled thermosetting resins having a free radical based cure chemistry are prepared for use as solder paste replacements for electrical conducting attachments of surface mount electronics components to printed circuit boards and as a die attach adhesive. The thermosetting resins exhibit rheological properties that allow them to be substituted for state-of-the-art solder paste and die attach adhesives. The conductor filled resins can be thermally cured in in-line processing operations to provide a low stress, substrate adherent, electrically conductive resin matrix.

17 Claims, No Drawings

Those and other objects of this invention are achieved by a conductor-filled thermosetting resin formulation comprising a free radical cross linkable polymer, a free radical initiating agent, and an unsaturated monomer capable of cross-linking the polymer. The cross-linking unsaturated monomer is preferably a bifunctional olefinic monomer having a boiling point greater than 200° C. at atmospheric pressure. The thermosetting resin of this invention optionally includes a low shrink or low profile thermoplastic resin to reduce shrinkage and concomitant internal stress in the cured resin. The resin formulations can be cured to form a shape-retaining electrically conducting resin matrix in less than 5 minutes, more typically less than 2 minutes, at a temperature of 200° C. or below. Physical and chemical properties of the resin formulations allow them to be used for die attachment and surface mount applications with little or no revision to existing manufacturing protocols.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention there is provided a thermosetting resin formulation which can be cured through a free radical cross-linking/polymerization mechanism to provide electrically conductive resin matrices. The present resin formulations are in the form of a thixotropic fluid/paste having rheological characteristics that will allow it to be substituted for state-of-the-art die attach and solder paste formulations.

Generally the resin formulations of this invention comprise a free radical cross-linkable polymer, an unsaturated monomer capable of cross-linking the polymer, a free radical initiating agent, and an electrically conductive microparticulate filler. In one preferred embodiment, the present formulation further comprises a thermoplastic resin, most preferably a low shrink or low profile thermoplastic resin which functions to reduce post-cure stress in the cured electrically conductive matrix. Other optional additives can be employed to optimize chemical and rheological characteristics. For example, a small amount of a polymerization inhibitor can be added to enhance "open time" and shelf life. In addition, coupling agents can be added to improve "wetting" of the electrically conductive microcparticulate filler component and, as well, to improve adhesion characteristics of the cured conductive resin matrix.

The present formulations comprise about 15 to about 60 weight percent of a resin component. The resin component of the present formulation comprises about 30 to about 100 weight percent, more typically from about 30 to about 80 weight percent, and most preferably about 35 to about 75 weight percent of a free radical cross-linkable polymer. Such cross-linkable polymers include the commercially available thermosetting, unsaturated polyesters, vinyl esters, polybutadiene homopolymers and co-polymers having pendant 1,2-vinyl groupings, and other unsaturated pre-polymers prepared by partial polymerization of bifunctional olefinic monomers such as divinylbenzene, diallyl isopthlate or diallyl isopthalate, and other polymeric compounds having pendant unsaturated groups capable of undergoing free radical polymerization itself or co-polymerization with unsaturated monomer components. Most preferred of the free radical cross-linkable polymers are those that exhibit high free radical initiated cure rates in the presence of a monomer cross-linking agents. Vinyl esters and commercial polyesters prepared from maleic or fumaric acid with dihydric alcohols such as ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, dipropylene glycol or triethylene glycol are preferred reactive free radical cross-linkable polymers.

The resin composition of the present formulation is formulated to contain about 0 to about 70 weight percent of an unsaturated monomer capable of cross-linking the cross-linkable polymer. The monomer and the free radical cross-linkable polymer are selected so that they form a homogeneous mixture. The monomer is generally of the vinyl type (including at least one group —C=CH_2 in each molecule). Commercially available monomers include styrene, vinyl toluene, methyl methacrylate, methyl styrene, divinylbenzene, divinylpyridine, diallyl phthalate and diallyl isopthalate. Monomers exhibiting low vapor pressure (having a boiling point, for example, > 200° C.), are preferred. Bifunctional olefinic monomers are used to prepare preferred thermosetting resin formulations of the invention. Diallyl phthalate is most preferred. Its high boiling point and concomitant low volatility allows curing of the present resin formulations even in thin films without premature loss (evaporation) of the monomer component. There are commercially available liquid cross-linkable polymers, such as Ricon® brand high vinyl 1-2 vinyl liquid polybutadiene that are free radical cross-linkable without added monomer. Such polymers can be used neat as the sole resin component of the formulation or with minor amounts of monomer added only for viscosity control.

The present thermosetting resin formulation further comprises about 40 to about 85 weight percent, more preferably about 50 to about 80 weight percent, of an electrically conductive microparticulate filler. A wide variety of microparticulate fillers are commercially available. They include microparticulate metals including silver, gold, platinum, palladium, nickel and copper. The conductive microparticulate compositions can be in the form of powders, flakes, or coated metal, glass, or ceramic particles. The nature of the electrically microparticulate filler is not critical except to the extent that the filler should be used in a quantity and of a nature such that the cured resin has a resistivity of less than about 10^{-3} ohms per centimeter, preferably less than 10^{-5} ohms per centimeter. One electrically conductive microparticulate filler that has imparted favorable conductivity characteristics to the cured resin and, as well, favorable rheological properties to the pre-polymerized resin formulation is silver powder/flakes having a tap density > 3.0. In a most preferred thermosetting resin formulation of this invention, the electrically conductive microparticulate filler comprises silver flake having a tap density of > 4.0. Such high tap density silver flake is commercially available as product AX10C from Amepox Microelectronics Ltd. of Lodz, Poland. Thermosetting resin formulations of this invention that have performed particularly well in solder paste applications have been formulated using mixtures of the very high tap density silver flake with other silver particulates of somewhat lower tap density. It has been found that rheological characteristics of the resin formulation, for example the thixotropic index which is important for processability in many applications, can be adjusted by adjusting the ratio of high tap density and low tap density silver powder components.

One other component of the thermosetting resin formulation of the present invention is a free radical initiating agent. That component is added in an amount sufficient to promote short cure times for the thermosetting resin formulations at temperatures of about 200° C. or below. Preferably the free radical initiator is added in an amount effective to promote a short resin cure cycle—the resin formulation should cure to a shape-retaining electrical conductive matrix

Lupersol. Leguval® resins are thermoplastic resins available from DSM. The coupling agent A-187 silane is gamma-glycidoxypropyltrimeth xysilane, an epoxide functional coupling agent sold by Uni n Carbide. The silver powder/flakes identified as AX10C and AX20L are silver flake products available from Amepox. AX10C is a silver semi-flake product having a tap density of about 4.8 to about 5.6. AX20L is a silver flake product having a tap density of about 3.1 to about 3.6.

Several test resin compositions for use in the present conductor filled resin formulations were prepared to evaluate viscosity and cure time. The results of that test are shown in Table 1.

TABLE 1

Formula	Composition/pbw		Viscosity/Brookfield #4, 10 rpm, 25° C. (cP)	Cure Time (average) 150° C. (sec)	175° C. (sec)
A 331	Hetron 912/65 pbw DAP/35 pbw Catal. 331/2 pbw		4700	17.5	13.4
B 575	Hetron 912/65 pbw DAP/35 pbw Catal. 575/2 pbw		4560	11.5	9.3
E 256	Hetron 912/65 pbw DAP/35 pbw Catal. 256/2 pbw		5560	8.2	7.6
L 575	Hetron 912/65 pbw DAP/35 pbw	65 pbw	9200	17.6	17.6
	Leguval KU3-17248/50 pbw DAP/50 pbw	35 pbw			
	Catal. 575/2 pbw				
LK 575	Hetron 912/65 pbw DAP/35 pbw	65 pbw	5000	16.8	16.2
	Leguval KU3-17248/60 pbw DAP/40 pbw	35 pbw			
	Catal. 575/2 pbw				

Each of Formulas A331, B575, and L575 were used to prepare silver filled resin formulations in accordance with the present invention. The resin formulations were prepared by blending the silver flake components into the prepared resin compositions. The data obtained upon assessment of the chemical and physical properties of the silver filled formulations is shown in Table 2.

TABLE 2

FORMULA		Initial Viscosity Stand. Brookfield #7, 2.5 rpm, 25° C.	Thixotropic Ratio (1:10 rpm)	Shrinkage Test mm (*)	Resistance (**)	Lap Shear (*)
A 331 AX10C AX20L	-100 pbw -350 pbw -100 pbw	154 000	3.7	0.734	0.12 ohm	-1100
B 575 AX10C AX20L	-100 pbw -350 pbw -100 pbw	163 000	3.9	0.64	0.12 ohm	—
L 575 AX10C AX20L	-100 pbw -250 pbw -100 pbw	325 000	2.2	0.0	0.1 ohm	-600

*Curing 175° C. — 15 minutes — For stimulation long term work.
**Curing 175° C. — 2-3 minutes — After this time was no change of resistance.

A resin formulation having the following formula was prepared as a solder paste replacement.

SOLDER PASTE	
Hetron 912 Resin	42.25
DAP Monomer	36.75
**Leguval 7232B Solids	21.00
*Hydroquinone Solution	0.05
Lupersol 575-P75	2.00
5.30 Tap Density Silver	204.00
3.35 Tap Density Silver	204.00

-continued

A-187 Silane	0.38
	510.43